Sulfur-Tolerant Pd/Cu and Pd/Au Alloy Membranes for H_2 Separation with High Pressure CO_2 for Sequestration

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Objectives

- To test Pd/Cu membranes with an FCC alloy on the top layer for H_2S tolerance by investigating the H_2 permeance decline and recovery and reversibility of the poisoning
- To examine the surface morphology of the Pd/Cu membranes after H_2S exposure
- To investigate galvanic displacement of Pd by Au as a method to produce Pd/Au alloy membranes
- To characterize the Pd/Au alloy membranes

Introduction

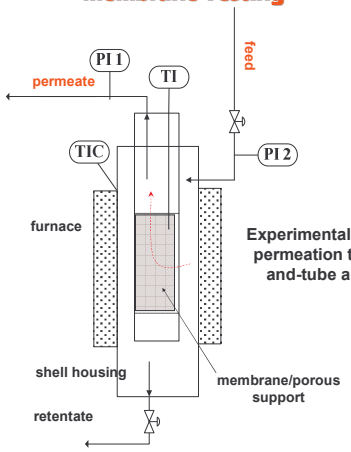
When diffusing through a Pd membrane, H_2 adsorbs, dissociates, and then diffuses through the Pd. However, H_2S poisons Pd membranes, decreasing the H_2 permeance. Pd/Cu and Pd/Au alloys have been shown to be more tolerant to H_2S than pure Pd. Pd/Au alloys are known to have a higher permeance than pure Pd. Pd/Cu alloys have a lower permeance in the FCC phase, therefore a Pd/Cu alloy was synthesized on the top layer of the Pd membrane.

Experimental

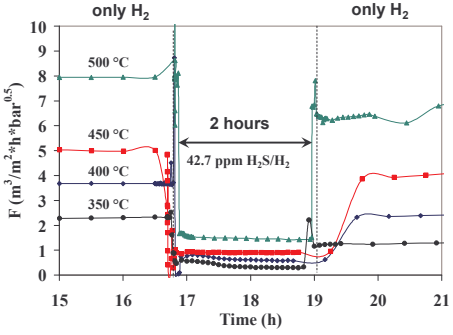
Membrane/Coupon Synthesis

- Pd electrolessly deposited on tubular porous Inconel supports (membrane area = 24 cm^2) and porous stainless steel coupons
- Cu layer electrolessly deposted on Pd
- Au layer deposited by galvanic displacement of Pd in a $NaAu(Cl)_4 \cdot 2\ H_2O$ solution
- Annealing performed in H_2

Membrane Testing



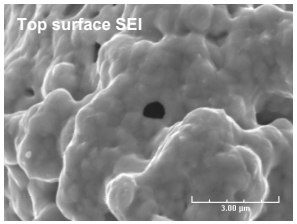
Experimental apparatus for permeation testing, shell-and-tube arrangement



H_2 permeance decline during H_2S exposure

Pd/Cu: SEM/EDX analysis, 19 wt % Cu

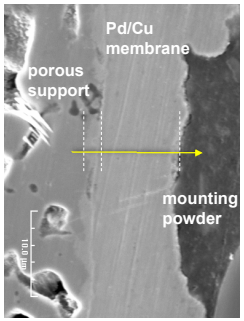
SEM micrographs of surface (top) and cross section (bottom)

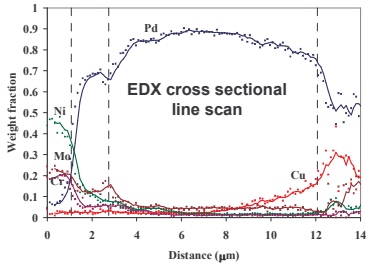


19 wt % Cu membrane was tested for over 2000 hours at 250 – 500 °C and exposed to H_2S at 400 and 450 °C

Dotted lines in micrograph correspond to dotted lines in line scan which represent the interfaces

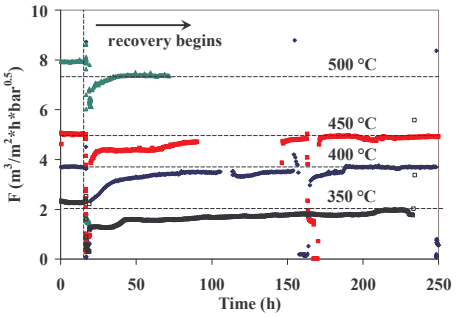
Approximately 25 wt % Cu is present on surface



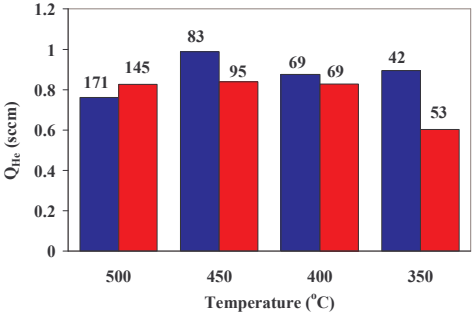


Results

Pd/Cu: Sulfur testing, 8 wt % Cu

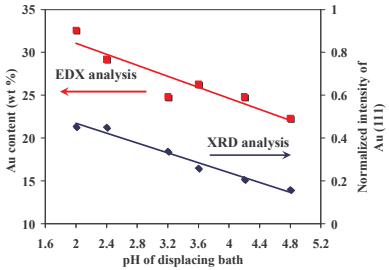


H_2 permeance recovery after reintroducing pure H_2



He leak (y-axis) and ideal H_2/He separation factor (above bars) before (blue) and after (red) H_2S exposure

Pd/Au: Galvanic displacement



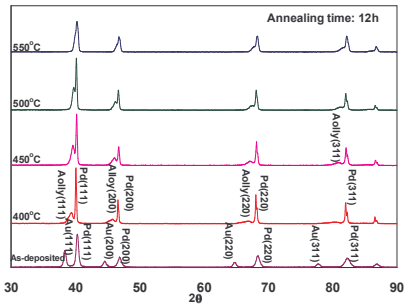
Dependence of Au concentration in deposit on bath pH

$Pd(Cl)^{2-} + 2e^- = Pd^0 + 4Cl^-$ $E_0 = 0.62$ v

$Au(Cl)^- + 3e^- = Au^0 + 4Cl^-$ $E_0 = 1.0$ v

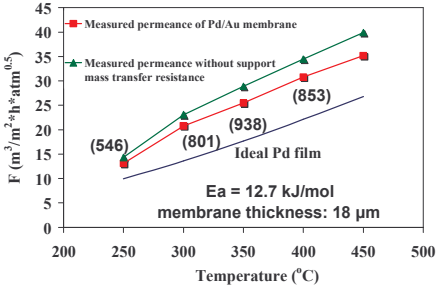
$2\ Au^{3+} + 3\ Pd^0 = 2\ Au^0 + 3\ Pd^{2+}$

Pd/Au: Alloy formation



XRD patters of coupons annealed in H_2 as a function of temperature

Pd/Au: Membrane characterization, 5 – 15 wt % Au



H_2 permeance as a function of temperature

Conclusions

Pd/Cu study

- Permeance decline with H_2S exposure had little dependence on temperature
- Recovery period increased with decreasing temperature
- H_2S poisoning partly irreversible at these conditions
- At temperatures below 500 °C, H_2S exposure decreased the He leak
- Cu gradient remained intact throughout testing period
- Sulfur compounds were not detected on surface
- Pinholes seen on surface

Pd/Au study

- Deposition rate of Au increased with decreasing pH
- Pd/Au alloy formed quickly at higher temperatures
- Pd/Au membrane had a higher permeance than pure Pd